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**Organic NLO Polymers. 5. Homopolymerization of Indole Based**

**NLO-phore: A Heterocycle  $\chi^{(2)}$  NLO Main-Chain Polymer**

by

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13. ABSTRACT (Maximum 200 words)  The paper describes the synthesis of main-chain NLOPs from indole-based NLO-phores/monomers. Homopolymers were prepared and spun cast into thin films. Corona poling of the samples produced materials which exhibited SHG signal (~1 pm/V) with enhanced stability in comparison to related guest/host systems.				
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# Organic NLO Polymers. 5. Homopolymerization of Indole Based NLO-phore: A Heterocycle $\chi^{(2)}$ NLO Main-Chain Polymer

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## Introduction

The design and synthesis of new NLO materials for optoelectronic device applications can be accomplished through a variety of schemes.<sup>1</sup> The development of polymeric  $\chi^{(2)}$  NLO materials has been approached from a variety of creative design strategies. The NLO-phore has been incorporated as a covalently bound moiety,<sup>2</sup> as a guest within a polymer host,<sup>3</sup> incorporated in the polymer backbone.<sup>4</sup> Most of these techniques require alignment of the NLO-phore by poling.<sup>5</sup>

In this communication, we present the synthesis of a dipolar main-chain NLO-polymer based on the indole<sup>6</sup> heterocycle donor-group and a study of NLO-phore orientation and relaxation using the techniques of corona poling and second harmonic generation.<sup>7</sup>

## Results and Discussion

**Monomer synthesis.** Treatment of 2-methylindole-3-carboxaldehyde with NaH followed by reaction with 6-iodohexanol in DMF affords 1 in 70% yield. Condensation of 1 with ethyl cyanoacetate in the presence of  $\text{Ti}(\text{O}i\text{Bu})_4$  results in a mixture of ethyl and butyl esters 2, 62% yield (Scheme D). This however, has no apparent disadvantage in the subsequent polymerization step.

**Polymer synthesis and Properties.** Monomer 2 is homopolymerized employing standard transesterification conditions (Scheme D). The resulting polymer has moderate molecular weight ( $M_n=15,000$ , Polydispersity = 4.8) and is soluble in common organic solvents. The amber polymer has a  $\lambda_{\text{max}}$  absorption in the region 390 nm. The DCS studies show the  $T_g$  to be 66 °C.

Polymer 3 is subjected to corona poling at  $T_g + 10$  °C, with the optical signal monitored during the entire process (Figure 1, maximum  $\chi^{(2)}$  of 0.72 pm/V).<sup>8</sup> When the polymer is corona poled at  $T_g + 10$  °C and then allowed to cool to ambient temperatures with the electric field applied, the signal is maintained for well over 130 h with a 50% loss at 8 h. When compared to guest-host systems<sup>9</sup> of similar size and dipole

moment, the response time is slower; however, the relaxation rate is also much slower (Figure D). It is worth noting that a main-chain NLO polymer very recently prepared by the homopolymerization of a monomer in the presence of an electric field (corona poling) also displays a relatively rapid loss of SHG signal (~40%) after removal of the electric field at ambient temperature.<sup>9</sup>

Scheme I

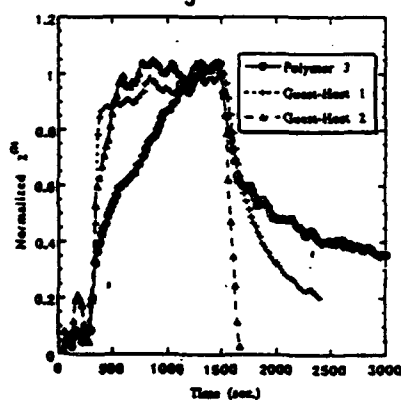
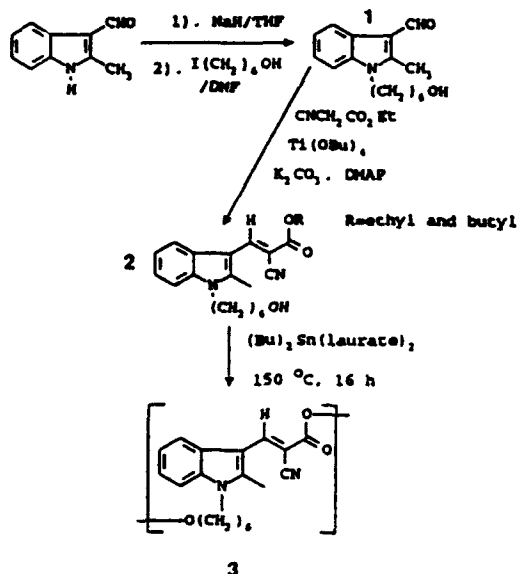


Figure 1. Normalized  $\chi^{(2)}$  signals of polymer 3 (o) and guest-host systems 4-hydroxy-3,5-bis(MeO) $\text{C}_6\text{H}_3\text{CH}=\text{C}(\text{CN})\text{CO}_2\text{Et}$  (+) and 4-(HO(CH<sub>2</sub>)<sub>6</sub>O)-3,5-bis(MeO) $\text{C}_6\text{H}_3\text{CH}=\text{C}(\text{CN})\text{CO}_2(\text{CH}_2)_6\text{OH}$  (Δ) in PMMA.

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## Concluding Remarks

This work illustrates that indole based dipolar polymers fall into a class of NLO main-chain polymers which are aligned by corona poling as evidenced by measurement of the SHG signal. More details of the optical characterization will be presented shortly.<sup>10</sup>

## Experimental Section

**Preparation of 3-(butyl-( $\alpha$ -cyano acrylate))-1-(N)-(6-hydroxyhexyl)-2-methyl indole (2).** A Schlenk flask was charged with 1 (2.0 g, 7.7 mmol), excess  $K_2CO_3$  (4.0 g, 28.9 mmol),  $CHCl_3$  (40 mL),  $CNCH_2CO_2Et$  (1.0 g, 9.2 mmol),  $Ti(OBu)_4$  (2.6 g, 7.7 mmol), DMAP (150 mg, 1.2 mmol) and allowed to react at 55 °C for 22 h. The mixture was extracted with ether (125 mL). The solvents were removed under reduced pressure and further purification was accomplished by column chromatography. Aluminum oxide deactivation was done with MeOH in  $CH_2Cl_2$  (1/10, v/v) and elution with MeOH in  $CH_2Cl_2$  (1/20, v/v). The first broad yellow band was collected and solvents were removed under reduced pressure to afford 2 (1.7 g, 62%).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  8.51 (s, H, =CH), 8.17 (m, 2 H, Ar), 7.27 (m, 2 H, Ar), 4.34 (t,  $J=6.6$  Hz, 2 H,  $CH_2N$ ), 4.14 (m, 2 H,  $OCH_2(CH_2)_5$ ), 4.17 (t,  $J=7.5$  Hz, 2 H,  $CH_2O_2C$ ) 3.62 (t,  $J=6.0$  Hz, 2 H,  $CH_2OH$ ), 2.59 (s, 3 H,  $CH_3$ ), 1.80-1.26 (m, 4 H,  $CH_2$ 's);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  164.9 ( $CO_2$ ), 148.3 ( $=C(CN)CO_2$ ), 148.3, 125.4 (Ar C), 123.3, 123.2, 122.1, 109.4 (Ar CH), 118.0 (CN), 109.9 (=CH), 137.2 (indole- $C_2$ ), 118.0 (indole- $C_3$ ), 65.7 ( $OCH_2$ ), 44.0 ( $CH_2N$ ), 32.4, 30.6, 30.3, 29.5, 26.7, 26.6, 25.4 ( $CH_2$ 's), 14.3, 13.7 ( $CH_2CH_2$ 's), 12.1 ( $CH_3$ ); IR ( $CH_2Cl_2$ )  $\nu_{max}$  1712  $cm^{-1}$ .

**Preparation of [(3=CH)-2-methylindole-1-( $CH_2$ )<sub>6</sub>CO<sub>2</sub>C(CN)=)] (3).** A Schlenk tube was charged with a  $CH_2Cl_2$  (5 mL) solution of 2 (1.0 g, 2.8 mmol) and  $[CH_3(CH_2)_6CO_2]_2Sn[(CH_2)_6CH_2]_2$  (12.52 mg, 0.02 mmol). The solvent was removed under reduced pressure and the mixture was heated in an oil bath at 140 °C for 22 h. Polymer was precipitated from  $CH_2Cl_2$ /pentane to afford an orange solid 3 (0.66 g, 82%).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  8.53 (s, H, =CH), 8.24-8.22 (m, 2 H, Ar), 7.33 (m, 2 H, Ar), 4.32 (m, 2 H,  $OCH_2$ ), 4.17 (m, 2 H,  $CH_2N$ ), 2.6 (s, 3 H,  $CH_3$ ), 1.89-1.29 (m, 8 H,  $CH_2$ 's);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  164.8 ( $CO_2$ ), 148.3 ( $=C(CN)CO_2$ ), 148.3, 125.3 (Ar C), 123.3, 123.2, 122.3 109.4 (Ar CH), 117.9 (CN), 109.8 (=CH), 137.1 (indole- $C_2$ ), 118 (indole- $C_3$ ), 65.7 ( $OCH_2$ ), 44.0 ( $CH_2N$ ), 30.7, 29.5, 28.4, 26.7 ( $CH_2$ 's), 12.1 ( $CH_3$ ); IR ( $CH_2Cl_2$ )  $\nu_{max}$  1712  $cm^{-1}$ . Anal. Calcd for  $[C_{25}H_{30}O_2N_2]_n$ : C, 74.02; H, 6.49. Found: C, 73.37; H, 7.46.

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